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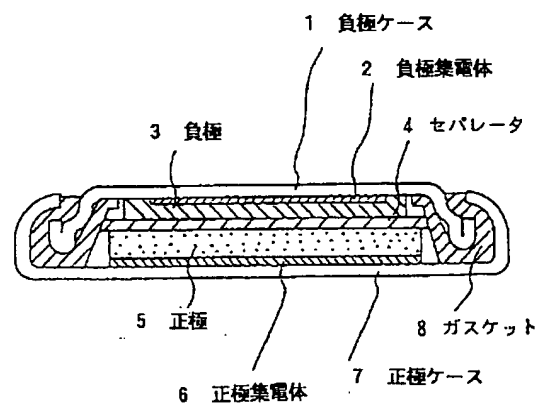
(54)【発明の名称】 非水電解質二次電池及びその製造方法

(57)【要約】

【目的】 高電圧、高エネルギー密度で充放電特性が優れ、且つサイクル寿命の長い新規な非水電解質二次電池及びその製造方法。

【構成】 負極と正極とリチウムイオン導電性の非水電解質とから少なくとも成る非水電解質二次電池において、正極活物質としてリチウム遷移金属複合酸化物もしくはリチウムホウ素遷移金属複合酸化物、負極活物質としてマンガンとリチウムの複合酸化物を用いる。

【効果】 負極と正極が共に充放電容量が大きく、かつ充放電時の分極（内部抵抗）が小さいため、高電圧高エネルギー密度で且つ大電流充放電特性に優れると共に、過充電過放電による劣化が小さく、サイクル寿命の長い二次電池が得られる。



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# PATENT ABSTRACTS OF JAPAN

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## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY AND ITS MANUFACTURE

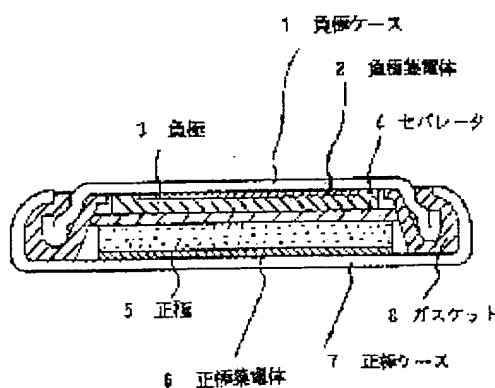
(57)Abstract:

PURPOSE: To provide a new nonaqueous electrolyte secondary battery having high voltage and a high energy density, excellent in charge/discharge characteristics, and having a long cycle life and pride a manufacturing method therefor.

CONSTITUTION: A nonaqueous secondary battery is constituted of at least a negative electrode 3, a positive electrode 5, and a lithium ion conducting nonaqueous electrolyte. A lithium transition metal composite oxide or a lithium-boron transition metal composite oxide is used for a positive electrode active material, and a manganese-lithium composite oxide is used for a negative electrode active material.

Charge/discharge capacities of the negative electrode 3 and the positive electrode 5 are large, the polarization (internal resistance) at the time of charge/discharge is small, and the secondary

battery having high voltage and a high energy density, excellent in large-current charge/discharge characteristics, and having little deterioration due to overcharge/ overdischarge and a long cycle life can be obtained.



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## CLAIMS

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[Claim(s)]

[Claim 1] It sets to the nonaqueous electrolyte rechargeable battery which consists of a negative electrode, a positive electrode, and the nonaqueous electrolyte of lithium ion conductivity at least, and is a formula (1).

$\text{Li}_x\text{M}_y\text{B}_z\text{O}_2$  (1)

(-- however, M -- transition metals -- it is -- x1, y, and z -- respectively --  $0 < x$  -- the positive electrode which uses as an active material the lithium transition-metals multiple oxide of the layer structure or lithium boron transition-metals multiple oxide shown by  $1 \leq x \leq 1.15$ ,  $0.85 \leq y+z \leq 1.3$ , and  $0 \leq z$ ), and a formula (2)

$\text{Li}_x\text{Mn}_2\text{O}$  (2)

The nonaqueous electrolyte rechargeable battery characterized by using the negative electrode which uses as an active material the multiple oxide of the manganese Mn shown by (however,  $0 \leq x \leq 2$ ), and Lithium Li.

[Claim 2] The manufacture approach of the nonaqueous electrolyte rechargeable battery according to claim 1 which is in an after [ cell assembly ] cell, or is characterized by depending on an electrochemical reaction with the matter containing manganese monoxide MnO, a lithium, or a lithium, making manganese monoxide MnO contain a lithium, and obtaining the multiple oxide of manganese and a lithium within a cell and out of a cell in the way of a cell production process.

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This invention uses as a negative-electrode active material and positive active material the matter which can occlusion emit a lithium, and about the nonaqueous electrolyte rechargeable battery using the nonaqueous electrolyte of lithium ion conductivity, especially, they are a high voltage and a high energy consistency, and a charge-and-discharge property is excellent, and it relates to the new long rechargeable battery of a cycle life.

[0002]

[Description of the Prior Art] The nonaqueous electrolyte cells using a lithium as a negative-electrode active material are a high voltage and a high energy consistency, and are already widely used as power sources the object for memory-backup, for cameras, etc. as a primary cell with the advantage of \*\* -- self-discharge is small excellent in dependability over a long period of time. However, with remarkable development of the electronic equipment of a pocket mold, communication equipment, etc., the device which requires a high current output from the cell as a power source appears variously, from a viewpoint of the formation of small lightweight of economical efficiency and a device, re-charge and discharge are possible, and the rechargeable battery of a high energy consistency is demanded strongly in recent years. for this reason, although the researches and developments which advance rechargeable battery-ization of said nonaqueous electrolyte cell which has a high energy consistency are done actively and put in practical use in part, energy density, a charge-and-discharge cycle life, dependability, etc. are \*\*\*\* -- it is \*\* -- it is inadequate.

[0003] Conventionally, as positive active material which constitutes the positive electrode of this kind of rechargeable battery, it depends on the gestalt of a charge-and-

discharge reaction, and the thing of three sorts of following types is found out. The 1st type is types which only a lithium ion (cation) depends on an intercalation, a day intercalation reaction, etc., and go in and out between the layers of a crystal, and between a grid location or an interstice, such as a metal chalcogen compound of  $\text{TiS}_2$ ,  $\text{MoS}_2$ , and  $\text{NbSe}_3$  grade, and a metallic oxide of  $\text{MnO}_2$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{LiXCoO}_2$  and  $\text{LiXNiO}_2$ , and  $\text{Li}_x\text{Mn}_2\text{O}_4$  grade, like \*\*. The 2nd type is a type like conductive polymers, such as the poly aniline, polypyrrole, and poly para-phenylene, with which only an anion mainly depends and frequents stability at a dope and a dedope reaction. The 3rd type is types (an intercalation, a day intercalation or a dope, dedope, etc.) with which both lithium cations and anions like \*\*, such as conductive polymers, such as intercalated graphite and the poly acene, can go in and out.

[0004] As a negative-electrode active material which, on the other hand, constitutes the negative electrode of this kind of cell, although the output voltage as a cell which the case where a metal lithium was used independently combined with the positive electrode using the above positive active material since electrode potential was \*\* most was the highest and the energy density was also highly desirable, in connection with charge and discharge, the dendrite and the non-\*\*\*\* compound generated on the negative electrode, degradation by charge and discharge was large, and there was a problem that a cycle life was short. In order to solve this problem, as a negative-electrode active material The alloy of (1) lithium and other metals, such as aluminum, Zn, Sn, Pb, Bi, and Cd, (2) --  $\text{WO}_2$ ,  $\text{MoO}_2$ , and  $\text{Fe}_2\text{O}_3$  and  $\text{TiS}_2$  etc. -- an inorganic compound and graphite -- The intercalation compound which carried out occlusion of the lithium ion into crystal structures of \*\*, such as a carbonaceous ingredient which calcinates the organic substance and is obtained, or an insertion compound, (3) Using the matter which can occlusion emit the lithium ion of \*\*, such as conductive polymers which doped the lithium ion, such as the poly acene and polyacetylene, is proposed.

[0005]

[Problem(s) to be Solved by the Invention] However, generally, since the electrode potential of these negative-electrode active materials is \*\* from the electrode potential of a metal lithium when a cell is constituted combining \*\*, the negative electrode using the matter which can occlusion emit lithium ions other than the above metal lithiums as a negative-electrode active material, and the positive electrode using the above positive active material, there is a fault of falling considerably from the case where the operating potential of a cell uses a metal lithium independently as a negative-electrode active material. For example, in using a lithium and alloys, such as aluminum, Zn, Pb, Sn, Bi, and Cd, at 0.2-0.8V, and a carbon-lithium intercalation compound, 0.5 - 1.5V operating potential falls with the lithium ion insertion compound of 0-1V,  $\text{MoO}_2$ , or  $\text{WO}_2$  grade.

[0006] Moreover, since elements other than a lithium also turn into a negative-electrode component, the capacity and energy density per volume and per weight fall remarkably. furthermore, when the alloy of the above-mentioned lithium of (1) and other metals is used The use effectiveness of the lithium at the time of charge and discharge is low, and a crack occurs in an electrode by the repeat of charge and discharge, and there is a problem that a cycle life is short, for producing a crack etc. In the case of the lithium intercalation compound of (2), or an insertion compound There is degradation of collapse of the crystal structure, generation of the irreversible matter, etc. by fault charge and discharge. Moreover, since there is much what has high (it is \*\*\*\*) electrode potential, There is a

fault that the output potential of the cell using this is low, and in being the conductive polymer of (3), there is a problem that charge-and-discharge capacity, especially the charge-and-discharge capacity per volume are small.

[0007] For this reason, in order to be a high voltage and a high energy consistency, and for a charge-and-discharge property to be excellent and to obtain the long rechargeable battery of a cycle life, the larger negative-electrode active material of the amount, i.e., effective charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly [ there is no degradation of collapse of a crystal structure, generation of the irreversible matter, etc. to which the electrode potential to a lithium depends on occlusion emission of the lithium ion at the time of charge and discharge low (it is \*\*\*\*), and ] is required.

[0008] On the other hand, in the above-mentioned positive active material, the 1st type has overcharge and the fault that degradation by collapse of a crystal, generation of the irreversible matter, etc. is large if overdischarge is carried out, although energy density is generally large. Moreover, by the 2nd and 3rd type, there is a fault that capacity and energy density are conversely small.

[0009] For this reason, in order a overcharge property and an overdischarge property are excellent and to obtain the rechargeable battery of high capacity and a high energy consistency, the larger positive active material of the amount which can carry out occlusion emission of the lithium ion reversibly [ there are no collapse of a crystal and generation of the irreversible matter which depend on overcharge overdischarge, and ] is required.

[0010]

[Means for Solving the Problem] This invention is an active material of the positive electrode of this kind of cell, in order to solve the above troubles.  $\text{Li}_x\text{M}_y\text{B}_z\text{O}_2$  of the aforementioned (1) formula (1)

(-- however, M -- transition metals -- it is --  $x_1$ , y, and z -- respectively --  $0 < x$  -- the lithium transition-metals multiple oxide of the layer structure or lithium boron transition-metals multiple oxide shown by  $1 \leq 1.15$ ,  $0.85 \leq y+z \leq 1.3$ , and  $0 \leq z$ ) -- using -- and -- as the active material of a negative electrode --  $\text{Li}_x\text{MnO}$  of the aforementioned (2) formula (2)

It raises using the multiple oxide of the manganese Mn shown by (however,  $0 \leq x_2$ ), and Lithium Li.

[0011] The lithium transition-metals multiple oxide or lithium boron transition-metals multiple oxide used as positive active material of this invention cell is compoundable as follows. That is, salts, such as each simple substance of Lithium Li, transition metals M, and boron B or each oxide, a hydroxide or a carbonate, and a nitrate, are mixed by the predetermined ratio, and, therefore, it is obtained by the temperature more than 600-degreeC in an ambient atmosphere which has the inside of air, or oxygen, and carrying out heating baking at the temperature of 700-900-degreeC preferably. When using those oxides or the compound which has oxygen as sources of supply, such as Li, M, and B, it is also possible to carry out heating composition in an inert atmosphere. Although heating time is usually enough in 4 - 50 hours, in order to promote a synthetic reaction and to raise homogeneity, it is effective to repeat the process of baking, cooling, and grinding mixing several times.

[0012] In a formula (1), although stoichiometric presentation  $x_1=1$  is a criterion in the

above-mentioned heating composition, as for the amount  $x_1$  of Li(s),  $0 < x_1 \leq 1.15$  are possible by an electrochemical intercalation, a day intercalation, etc. in which about 15% of indeterminate ratio presentation is also possible. As transition metals M, Co, nickel, Fe, Mn, Cr, V, etc. are desirable, the charge-and-discharge property is excellent in especially Co and nickel, and they are desirable. As the amount  $z$  of boron, and an amount  $y$  of transition-metals M, the effectiveness to reduction of polarization at the time of charge and discharge (internal resistance), the improvement in a cycle property, etc. is remarkable in  $0 \leq z$  and  $0.85 \leq y+z \leq 1.3$ , and it is desirable. On the other hand, since it will fall conversely if the charge-and-discharge capacity for every cycle has too many amounts  $z$  of boron, and it serves as max in  $0 < z \leq 0.5$ , especially this range is desirable.

[0013] As the desirable manufacture approach of this multiple oxide of the manganese and the lithium which are used as an active material of the negative electrode of this invention cell, although two kinds of following approaches are raised, limitation is not carried out to these. A primary method is the approach of heating and compounding in the ambient atmosphere which mixed the compound which has the above-mentioned manganese, the simple substances of a lithium, or those oxygen by the predetermined mole ratio, and controlled the inside of an inert atmosphere or a vacuum, or the amount of oxygen. What is necessary is just the compound which heats in the inert atmosphere of \*\*, such as a salt or organic compounds, such as each oxide, a hydroxide or a carbonate, and a nitrate, or a vacuum, and generates an oxide as each compound of the manganese used as a start raw material, and a lithium. Although heating temperature changes also with a start raw material and heating ambient atmospheres, it can be compounded above 400-degreeC and is more preferably good more than 600-degreeC preferably. [ of the temperature more than 700 degreeC ]

[0014] Thus, the multiple oxide of the manganese and the lithium which are obtained Remaining as it is or after processing a grinding particle size regulation, a granulation, etc. as occasion demands, can use this as an active material of a negative electrode, and Moreover, it depends on an electrochemical reaction with the matter containing the multiple oxide, metal lithium, or lithium containing this lithium of manganese like the second following approach. It depends on carrying out occlusion of the lithium ion to this multiple oxide further, or making a lithium ion emit from this multiple oxide conversely, and what increases or decreased the lithium content may be used as an active material.

[0015] The second approach is an approach of depending on an electrochemical reaction with the matter containing manganese monoxide MnO, a lithium, or a lithium, carrying out occlusion of the lithium ion to MnO, and obtaining the multiple oxide of manganese and a lithium. As matter containing the lithium for using for this electrochemical reaction, the matter which can occlusion emit a lithium ion which is used for positive active material or a negative-electrode active material raised by the term of the above-mentioned Prior art can be used, for example.

[0016] The occlusion of the lithium ion which depends on such an electrochemical reaction to MnO is in an after [ cell assembly ] cell, or can be performed within a cell and out of a cell in the way of a cell production process, and can specifically be performed as follows. What fabricated the mixture in the predetermined configuration is used as one electrode (operation pole). namely, mixing with (1) MnO or them, an electric conduction agent, a binder, etc. -- Make two electrodes the matter containing a metal lithium or a lithium counter in contact with the nonaqueous electrolyte of lithium ion conductivity as

another electrode (counter electrode), and an electrochemistry cell is constituted. How to energize or discharge with the suitable current for the direction in which an operation pole carries out a cathode reaction, and to carry out occlusion of the lithium ion to MnO electrochemically. It uses as an active material which constitutes a negative electrode by using this obtained operation pole as a negative electrode as it is, and a nonaqueous electrolyte rechargeable battery is constituted.

[0017] (2) mixing with MnO or them, an electric conduction agent, a binder, etc. -- fabricate a mixture in a predetermined configuration and include in a nonaqueous electrolyte rechargeable battery by using as a negative electrode what the alloy of a lithium or a lithium etc. was stuck by pressure or contacted to this, and carried out the laminating to it. The approach by which self-discharge of a kind of local battery is formed and carried out, and occlusion of the lithium is electrochemically carried out to MnO when this laminating electrode touches an electrolyte within a cell.

[0018] (3) Constitute a negative electrode for MnO as an active material of a negative electrode, contain a lithium in a positive electrode and constitute the nonaqueous electrolyte rechargeable battery using positive-active-material  $\text{Li}_x\text{MnBzO}_2$  of this invention which can occlusion emit a lithium ion. The approach by which occlusion of the lithium ion is carried out to MnO by performing charge or discharge as a cell at the time of use.

[0019] Thus, multiple oxide  $\text{Li}_x\text{MnO}$  of the manganese and the lithium which are obtained is used as an active material of a negative electrode. In a formula (2), the presentation ratio of Manganese Mn and Oxygen O produces the non-stoichiometric compound which often depends on the deficit of Manganese Mn or Oxygen O on the occasion of composition although 1:1 is a criterion as mentioned above, and the range of the deficit reaches to  $\pm 25\%$ . The thing of such an indeterminate ratio presentation is also contained in this invention. Moreover, especially the range of  $0 \leq x \leq 2$  is [ that what is necessary is just the range where this multiple oxide exists in stability as content  $x$  of a lithium ] desirable.

[0020] On the other hand as an electrolyte, gamma-butyrolactone, propylene carbonate, Ethylene carbonate, butylene carbonate, dimethyl carbonate, Diethyl carbonate, methyl formate, 1, 2-dimethoxyethane, independent or the mixed solvent of organic solvents, such as a tetrahydrofuran, dioxolane, and dimethyl formamide, -- as a supporting electrolyte --  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiCF}_3\text{SO}_3$  etc. -- the organic electrolytic solution which dissolved the lithium ion dissociative salt -- What is necessary is just nonaqueous electrolyte of lithium ion conductivity of  $\pm$ , such as inorganic solid electrolytes, such as a giant-molecule solid electrolyte which made said lithium salt dissolve to giant molecules, such as polyethylene oxide and the poly FOSUFAZEN bridge formation object, or  $\text{Li}_3\text{N}$ , and  $\text{LiI}$ .

[0021]

[Function] This invention is  $\text{Li}_x\text{MnBzO}_2$  to a negative-electrode active material about above  $\text{Li}_x\text{MnO}$  which can occlusion emit a lithium. By using for positive active material and using the nonaqueous electrolyte of lithium ion conductivity, it is a high voltage and a high energy consistency, and a charge-and-discharge property is excellent, and the new long rechargeable battery of a cycle life can be offered.

[0022] The negative electrode which uses as an active material multiple oxide  $\text{Li}_x\text{MnO}$  of the manganese and the lithium which depend on this invention has a large charge-and-



discharge capacity of the \*\*\*\* field whose electrode potentials to a metal lithium are 0-1.5V, and its degradation to which it depends on overcharge overdischarge is small, and it has the outstanding cycle property. Thus, although the reason the outstanding charge-and-discharge property is acquired is not necessarily clear, multiple oxide  $\text{Li}_x\text{MnO}_2$  of the manganese and the lithium which are the negative-electrode active material of this invention has the high mobility of the lithium ion in the inside of this structure, and since there are very many sites which can carry out occlusion of the lithium ion, it is presumed because occlusion emission of a lithium ion is easy.

[0023]  $\text{Li}_x\text{MyBzO}_2$  used as positive active material on the other hand The electrode potential to a metal lithium has about 4V or the high potential beyond it, and the reversible charge and discharge by the intercalation of Li ion and the day intercalation are possible among  $0 < x \leq 1.15$ , and degradation by overcharge overdischarge is small, and it has the outstanding cycle property. In  $0.05 \leq z < 0.5$ , the content z of boron B is small, and polarization is especially excellent in the cycle property. Thus, the reason the outstanding charge-and-discharge property is acquired is positive-active-material  $\text{Li}_x\text{MyBzO}_2$  of this invention, although it is not necessarily clear. Oxide  $\text{Li}_x\text{My}'\text{O}_2$  of the layer structure which does not contain B Since B is contained [ that some M atoms are permuted by B atom etc. and ] and a crystal structure and the electronic structure change, Li ion conductivity increases and it is presumed that it is because occlusion emission of a lithium ion becomes easy.

[0024] Therefore, greatly [ it is remarkable, the amount, i.e., the charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly, and ], since the cell using such negative-electrode active materials and positive active material has small polarization of charge and discharge, the charge and discharge in a high current are possible, degradation of decomposition, crystal collapse, etc. by overcharge overdischarge is hardly seen further, but it is very stable and shows the outstanding long property of a cycle life.

[0025] Hereafter, an example explains this invention to a detail further.

[0026]

[Example]

(Example 1) Drawing 1 is the sectional view of the coin mold cell in which an example of the nonaqueous electrolyte rechargeable battery which depends on this invention is shown. In drawing, 1 is a negative-electrode case which serves as a negative-electrode terminal, and carries out spinning of the plate made from stainless steel which carried out nickel plating of outside one side. 3 is the negative electrode constituted using the negative-electrode active material which depends on below-mentioned this invention, and is pasted up on the negative-electrode case 1 with the negative-electrode charge collector 2 which consists of electroconductive glue which makes carbon a conductive filler. 7 is the positive-electrode case made from stainless steel which carried out nickel plating of outside one side, and serves as the positive-electrode terminal. 5 is the positive electrode constituted using the positive active material which depends on below-mentioned this invention, and is pasted up on the positive-electrode case 7 with the positive-electrode charge collector 6 which consists of electroconductive glue which makes carbon a conductive filler. 4 is a separator which consists of a porosity film of polypropylene, and the electrolytic solution sinks in. a positive-electrode case opening edge bends it inside at the same time 8 is a gasket which makes polypropylene a subject, intervenes between the

negative-electrode case 1 and the positive-electrode case 7 and maintains the electric insulation between a negative electrode and a positive electrode -- having -- caulking \*\*\*\* -- therefore, cell contents are sealed and closed to things. An electrolyte is lithium perchlorate  $\text{LiClO}_4$  to volume ratio 1:1:2 mixed solvent of propylene carbonate, ethylene carbonate, and 1 and 2-dimethoxyethane. What was dissolvedl. one mol /was used. The magnitude of a cell was 1.6mm in the outer diameter of 20mm, and thickness.

[0027] The negative electrode 3 was produced as follows. What depended on the automatic mortar and carried out the grinding particle size regulation of the manganese monoxide  $\text{MnO}$  of 99.9% of commercial purity to the particle size of 53 micrometers or less is used as the negative-electrode active material which depends on this invention. It considers as a mixture. this -- as an electric conduction agent -- graphite -- as a binder -- bridge formation mold acrylic acid resin etc. -- the weight ratio 65:20:15 -- comparatively -- coming out -- mixing -- a negative electrode -- next, this negative electrode -- a mixture -- 2 ton/cm<sup>2</sup> After the diameter of 15mm and thickness carried out pressing to the pellet which is 0.23mm, what carried out heating under reduced pressure desiccation at 200 degrees C for 10 hours was used as the negative electrode.

[0028] The positive electrode 5 was produced as follows. Lithium-hydroxide  $\text{LiOH} \cdot \text{H}_2\text{O}$  and cobalt carbonate  $\text{CoCO}_3$  After having carried out weighing capacity so that the mole ratio of Li:Co might be set to 1:1, and mixing enough using a mortar, heating baking of this mixture was carried out at the temperature of 850 degrees C among atmospheric air for 12 hours, and the grinding particle size regulation was carried out to the particle size of 53 micrometers or less after cooling. Positive active material  $\text{LiCoO}_2$  which repeats this baking and a grinding particle size regulation twice, and depends on this invention It compounded.

[0029] this product -- positive active material -- carrying out -- this -- as an electric conduction agent -- graphite -- as a binder -- FU \*\*\*\* resin etc. -- the weight ratio 80:15:5 -- comparatively -- coming out -- mixing -- a positive electrode -- a mixture -- carrying out -- a degree -- this positive electrode -- a mixture -- 2 ton/cm<sup>2</sup> After carrying out pressing to a with a diameter thickness [ 0.67mm thickness of 16.2mm ] pellet, what carried out heating under reduced pressure desiccation at 100 degrees C for 10 hours was used as the positive electrode.

[0030] Thus, after neglect aging of the produced cell (it considers as Cell A) was carried out for one week at the room temperature, the below-mentioned charge and discharge test was performed. The charge-and-discharge property of 1 cycle eye when performing this cell A by 1mA constant current, and performing a charge-and-discharge cycle on condition that termination electrical-potential-difference 4.4V of charge and termination electrical-potential-difference 2.0V of discharge and a two-cycle eye was shown in drawing 2 , and the cycle property was shown in drawing 3 . In addition, the charge-and-discharge cycle was started from charge.

[0031] Lithium manganese multiple oxide  $\text{Li}_{1-x}\text{MnO}$  which a lithium ion is therefore emitted to charge into an electrolyte from positive active material, this lithium ion moves in the inside of an electrolyte, electrode reaction is carried out to a negative-electrode active material, and occlusion of the lithium ion is electrochemically carried out to an active material, and contains a lithium generates this cell A. Next, it depends on a lithium ion being emitted into an electrolyte from the lithium manganese multiple oxide of a negative electrode on the occasion of discharge, moving in the inside of an electrolyte,

and occlusion being carried out to positive active material, and charge and discharge can be repeatedly carried out to stability. Here, a negative-electrode active material forms multiple oxide  $\text{Li}_{x/2}\text{MnO}$  containing a lithium in the cycle of subsequent discharge-charge in addition to the time of full discharge, after generating multiple oxide  $\text{Li}_2\text{MnO}$  which contains a lithium by 1st charge.

[0032] The cell A by this invention is understood that charge-and-discharge capacity is remarkably large so that clearly from drawing 2 -3. Moreover, except 1 cycle eye, the fall of discharge capacity (charge-and-discharge effectiveness) to charge capacity is remarkably small, and its fall (cycle degradation) of the discharge capacity by the repeat of charge and discharge is also small. Furthermore, it crosses to all charge-and-discharge fields, and it turns out that the difference of the operating potential of charge and discharge is remarkably small, polarization (internal resistance) of a cell is remarkably small, and high current charge and discharge are easy.

[0033] In addition, the cause that the fall (initial loss) of the discharge capacity of 1 cycle eye to the charge capacity of 1 cycle eye is a little large In charge of 1 cycle eye, in case occlusion of the lithium ion is electrochemically carried out to a negative-electrode active material a negative electrode -- the side reaction generated between graphite, a binder, etc. which were added to the mixture as an electric conduction agent, and Li is the cause of main, and occlusion is carried out to MnO of a negative-electrode active material, and it thinks because Li which remains without being emitted at the time of discharge exists.

[0034] (Example 2) In drawing 1, the negative electrode 3 was produced as follows. the same negative-electrode active material as an example 1, and a negative electrode -- a mixture -- using -- 2 ton/cm<sup>2</sup> the lithium-negative electrode which stuck by pressure what carried out heating under reduced pressure desiccation at 200 degrees C for 10 hours, and pierced the given thickness Mino lithium foil in diameter of 14mm on it after the diameter of 15mm and thickness carried out pressing to the pellet which is 0.33mm -- a mixture -- the pellet laminating electrode was used as the negative electrode.

[0035] The positive electrode 5 was produced as follows. Lithium-hydroxide  $\text{LiOH}\cdot\text{H}_2\text{O}$ , cobalt carbonate  $\text{CoCO}_3$ , and boron oxide  $\text{B}_2\text{O}_3$  After having carried out weighing capacity so that the mole ratio of Li:Co:B might be set to 1:0.9:0.1, and mixing enough using a mortar, heating baking of this mixture was carried out at the temperature of 850 degrees C among atmospheric air for 12 hours, and the grinding particle size regulation was carried out to the particle size of 53 micrometers or less after cooling. Positive active material  $\text{LiCo}_{0.9}\text{B}_{0.1}\text{O}_2$  which repeats this baking and a grinding particle size regulation twice, and depends on this invention It compounded.

[0036] this product -- positive active material -- carrying out -- this -- as an electric conduction agent -- graphite -- as a binder -- FU \*\*\*\* resin etc. -- the weight ratio 80:15:5 -- comparatively -- coming out -- mixing -- a positive electrode -- a mixture -- carrying out -- a degree -- this positive electrode -- a mixture -- 2 ton/cm<sup>2</sup> After carrying out pressing to a with a diameter thickness [ 0.47mm thickness of 16.2mm ] pellet, what carried out heating under reduced pressure desiccation at 100 degrees C for 10 hours was used as the positive electrode.

[0037] Except [ all ] it, the cell A of an example 1 and the same cell B were produced. Thus, after neglect aging of the produced cell was carried out for one week at the room temperature, the below-mentioned charge and discharge test was performed. this aging -- the lithium-negative electrode of a negative electrode -- a mixture -- a pellet laminating

electrode touches nonaqueous electrolyte within a cell -- the lithium foil -- substantial -- all -- a negative electrode -- occlusion was electrochemically carried out to the mixture. [0038] Thus, about the obtained cell B as well as an example 1, the charge-and-discharge cycle trial was performed by 1mA constant current on condition that termination electrical-potential-difference 4.4V of charge, and termination electrical-potential-difference 2.0V of discharge. The charge-and-discharge property of 1 cycle eye at this time and a two-cycle eye was shown in drawing 4 , and the cycle property was shown in drawing 5 .

[0039] Drawing shows that the cell B of this example has the charge-and-discharge property which was excellent more than the cell A of an example 1 like [ it is \*\*\*\*\* and ]. Especially, there is almost no fall (initial loss) of the discharge capacity of 1 cycle eye to the charge capacity of 1 cycle eye, and it turns out that it is remarkably improved as compared with the cell A of an example 1. the lithium with which this is equivalent to a remained part to side reaction and MnO with an electric conduction agent, a binder, etc. accompanying charge and discharge -- beforehand -- a negative electrode -- carrying out a laminating to a mixture and making within an assembly and a cell describe the electrolytic solution for a cell -- after cell assembly -- spontaneous -- a negative electrode -- since this lithium was made to react to a mixture and occlusion was carried out to it, it is for the loss of the lithium in the negative electrode at the time of charge and discharge not to occur.

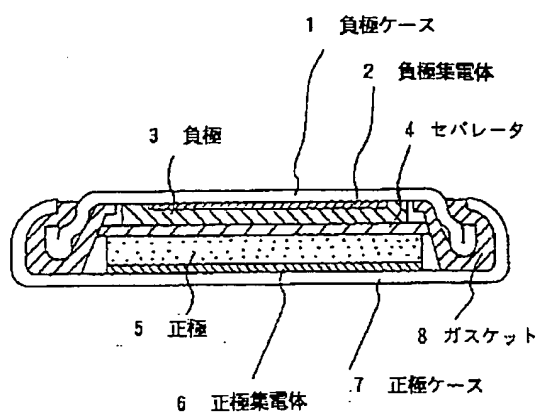
[0040] Moreover, by using the multiple oxide which contains boron as positive active material shows that cycle degradation is improved remarkably.

[0041]

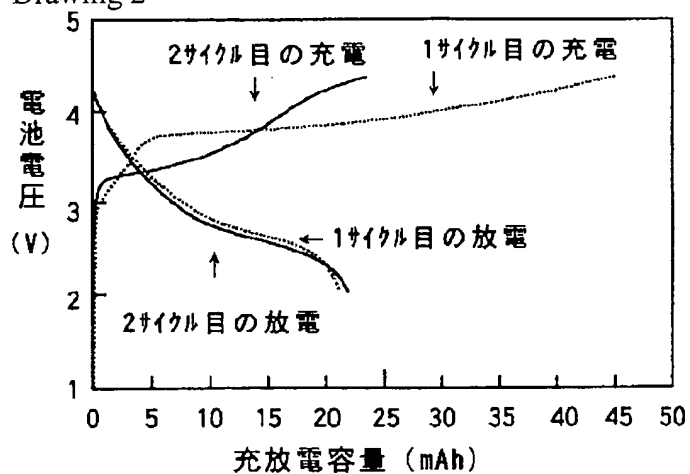
[Effect of the Invention] To the appearance explained in full detail above, this invention is lithium boron transition-metals multiple oxide  $\text{Li}_x\text{1MyBzO}_2$  as an active material of the positive electrode of a nonaqueous electrolyte rechargeable battery. It uses. Since [ remarkable, the amount, i.e., the charge-and-discharge capacity, which can carry out occlusion emission of the lithium ion reversibly by charge and discharge, using lithium manganese multiple oxide  $\text{Li}_x\text{2MnO}$  as an active material of a negative electrode, / large and ] polarization of charge and discharge is small, The charge and discharge in a high current are possible, and degradation of decomposition, crystal collapse, etc. by overcharge overdischarge is hardly seen further, but it has the \*\*\*\*\* effectiveness -- it is very stable and the cell of the long high voltage of a cycle life and a high energy consistency can be obtained.

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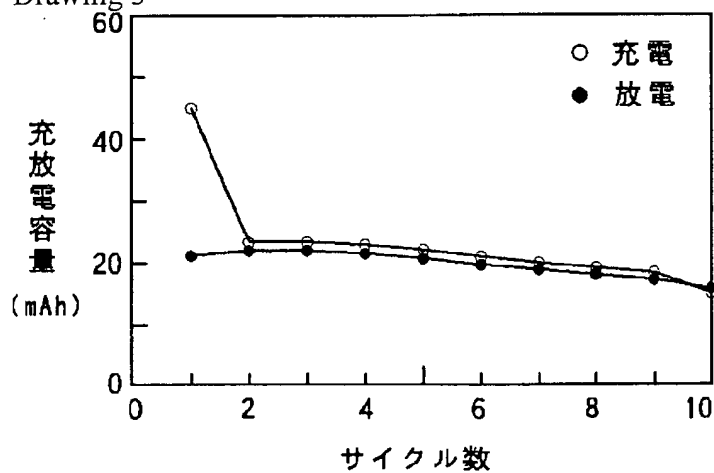
Drawing 1



Drawing 2



Drawing 3



Drawing 4

